Effect of surfactant concentration on the size of coated ferromagnetic nanoparticles

T. Prozorov[a,1], G. Kataby[a], R. Prozorov[b,2,*], A. Gedanken[a]

[a]*Department of Chemistry, Bar-Ilan University, Ramat-Gan, 52900 Israel*
[b]*Department of Physics, Bar-Ilan University, Ramat-Gan, 52900 Israel*

Abstract

We demonstrate that the average size of the coated ferromagnetic Fe_2O_3 nanoparticles is controlled by the surfactant concentration in the coating solution. Magnetization as a function of this ratio first increases and then decreases exhibiting a peak. Surface area of the coated material shows inverse behavior, i.e. first decreases and then increases. Both curves have extrema at the same ratio of surfactant/substrate. We explain these features in terms of competition between surface and volume contribution to the total energy, where surface contribution is determined by the bonding energy between the surfactant SH-group and Fe_2O_3. We support our conclusions by employing transmission electron microscopy and elemental analysis. © 1999 Elsevier Science S.A. All rights reserved.

1. Introduction

Nowadays, synthesis and study of materials consisted of nanometer-size particles are the subjects of intense research. Reduction of the particle size to a nanometer scale leads to a quantitative change in physical and chemical properties. Nanoparticles, both fine-crystalline and amorphous, have many important applications in magnetic recording, solar energy transformation, magnetic fluids, electronics, and chemical catalysis. Furthermore, small particles may be coated by different organic molecules, which form a chemical bond with the molecules on the particle surface. Such materials are considered to have potential applications in biological cell dissolution, in magnetic separation of minerals, as fillers in polymer matrices, and also for the removal of toxic elements from industrial wastes.

Several techniques have been developed for the preparation of ultrafine particles [1–10]. One of these techniques, sonochemistry, has been employed by Suslick and co-workers [11,12]. They demonstrated that by passing ultrasound radiation through $Fe(CO)_5$ or its solution in hydrocarbon solvents, 10-20 nanometer-sized particles of amorphous iron are obtained. Their research has been extended, and nanoparticles of Fe-Co alloy, a carbide Mo_2C, iron colloids [13,14], amorphous nickel [15], amorphous iron oxide [16], amorphous Fe-Ni alloy, and amorphous $NiFe_2O_4$ [17,18] were prepared. The amorphous nature of the particles was demonstrated by X-ray diffraction (XRD), as well as by electron-diffraction patterns [16]. All these amorphous materials were obtained as fine powder having nanometer-sized particles.

Self-assembled monolayer coatings (SAM) of various organic molecules on flat polished metallic and metal oxide surfaces have been extensively studied [19]. Fewer publications have described the synthesis and characterization of *SA* coatings on metal or on metal oxide powders. Among the few attempts is that of Liu and Xu, who coated nanosized magnetic particles (γ-Fe_2O_3) with 16-mercaptohexadecanoic acid, using a SA method [20]. The coating of the surface changes the intrinsic surface properties. In a few studies, the ratio of the amounts of surfactant to that of the metallic substrate was varied, and the average size of dispersed substance was determined as a function of this ratio[4,8,9,21–24]. Leff and his co-workers have demonstrated that the diameter of gold nanocrystals is dictated by the initial AuC_{14}^-/thiol ratio [24]. Davies et al. have noticed that the presence of varying amounts of oleic acid affects the growth of fine maghemite particles during the heating in alkali solution [22]. In all of these works, the

* Corresponding author. Tel.: + 1-217-244-4589; fax: + 1-217-333-9819; e-mail: ruslan@physics.uiuc.edu.
[1] School of Chemical Sciences, University of Illinois at Urbana-Champaign, 601 S. Goodwin Ave., Urbana, Illinois 61801, USA
[2] Present address: Loomis Laboratory of Physics, University of Illinois, Urbana-Champaign, 1110 W. Green St., Urbana 61801, USA
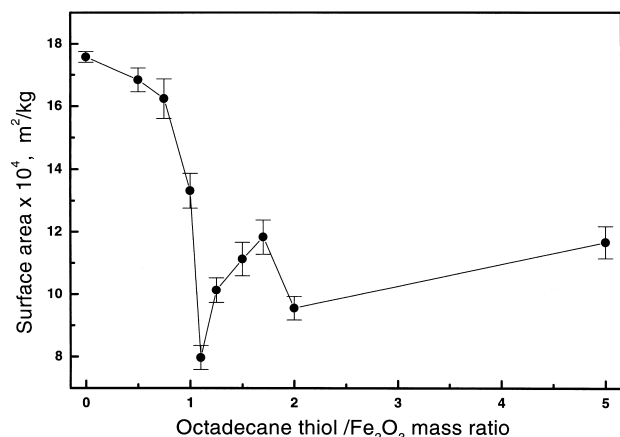
Fig. 1. Surface area vs. molar ratio of octadecanethiol/Fe$_2$O$_3$ in the coating solution.

general trend has been that the higher the amount of surfactant, the smaller the resulting particle. Yet, there is no information about controlling the given magnetic nanoparticle size in the coating process.

We have recently demonstrated that amorphous iron nanoparticles can be coated with organic molecules such as octadecyl trichlorosilane (*OTS*) or sodium dodecyl sulfate (*SDS*) [25,26]. Long chain thiols and alcohols now are added to the list of the previous molecules [27,28]. In the present study, we report on the preparation of amorphous nanosized Fe$_2$O$_3$, which was coated with octadecanethiol. This paper provides information on the characterization of the coated amorphous iron oxide nanoparticles by measuring their surface area, magnetization, and dependence on the surfactant/substrate ratio. A very strong dependence of the magnetic properties on the surfactant/Fe$_2$O$_3$ ratio is detected and interpreted in this manuscript.

2. Experimental

2.1. Sample preparation

The amorphous iron oxide (Fe$_2$O$_3$) nanoparticles were synthesized by sonochemical irradiation of a 1M solution of Fe(CO)$_5$ in decalin for 3 hours (Sonics and Materials, VC-600, Ti horn, 20 kHz, 100 W cm^{-2}). The irradiation took place in a glass flask open to the air [16]. The amorphisity of the particles was demonstrated by x-ray diffraction (XRD) [16]. The powder obtained was centrifuged and washed repeatedly with dry pentane and dried in a vacuum. Finally, the powder was annealed in a high vacuum (10^{-5} Torr) at 160–170°C in order to remove organic residue. Equal amounts of amorphous material were coated by different amounts of octadecanethiol (Aldrich, 98% purity, without further purification) with surfactant/oxide molar ratios of 0.3/1, 0.4/1, 0.5/1, 0.6/1, 0.7/1, 0.8/1, 0.9/1, 1.0/1, 1.1/1 and 3/1, respectively. The coating was always carried out on a powder obtained from one sonication batch, ensuring the reliability of the results. The Fe$_2$O$_3$ powder was dispersed in ethanol (absolute), and after the addition of the octadecanethiol, the suspension was agitated for 2 h. The coated particles were then washed extensively in ethanol, centrifuged, and dried in a vacuum at room temperature.

2.2. Characterization and analysis

The coated particles were subjected to FT-IR, thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), and surface area and magnetization measurements. These measurements were carried out for each molar ratio of the octadecanethiol/Fe$_2$O$_3$ and are reported elsewhere. In the same paper, we have presented the results of our study of
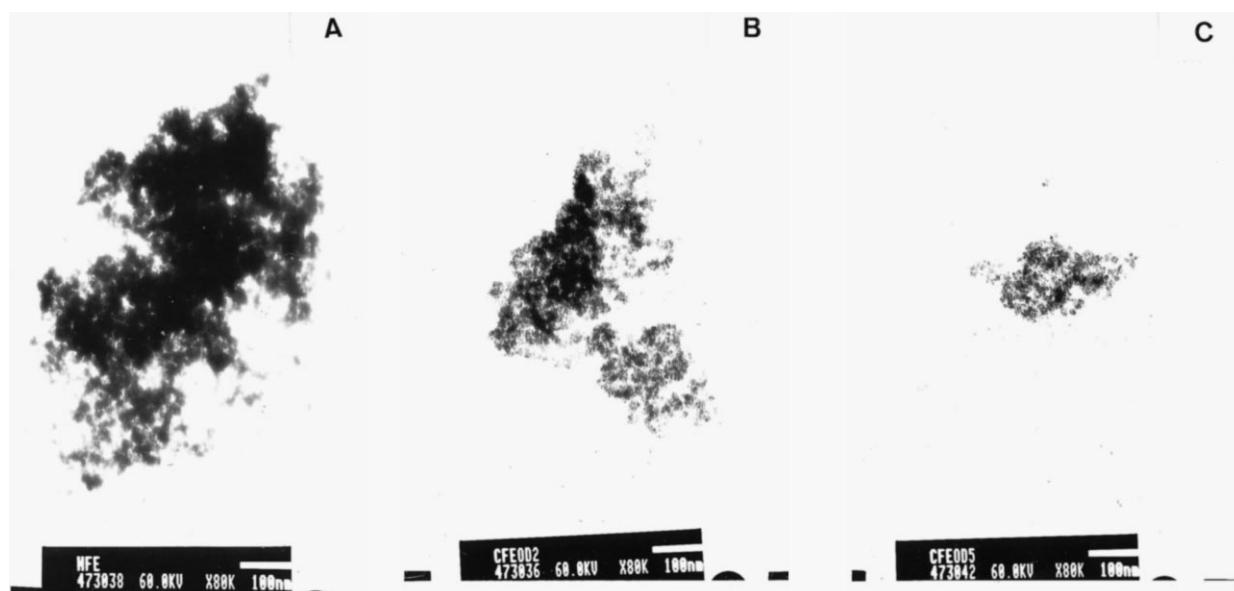

Fig. 2. TEM pictures of different octadecanethiol coated samples. The molar ratio of the thiol/Fe$_2$O$_3$ in the coating solution was: (a) 0.6/1, (b) 0.3/1, (c) 6/1.
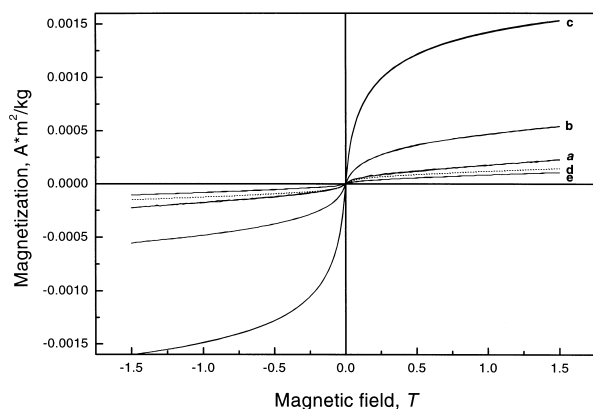
Fig. 3. Magnetization loops for (a) amorphous non-coated Fe_2O_3, the direct product of the sonochemical irradiation; for coated Fe_2O_3 with the molar ratio of the thiol/Fe_2O_3 in the coating solution: (b) 0.3/1, (c) 0.6/1, (d) 0.7/1, (e) 1/1.

the thermal stability of SA monolayer coatings [27]. The XRD of thiol-coated nanoparticles was re-measured and was found to be featureless indicating that the particles are either amorphous or too small to generate constructive diffraction.

Fig. 1 shows the results of the surface area measured by the BET method (Brunauer, Emmett and Teller), using N_2 as the absorbate (Micromeritrics Gemini III 2375). The minimal value of the surface area corresponds to an octadecanethiol/Fe_2O_3 molar ratio of 0.6/1. To examine whether this dependence is related to the structural modification of the coated particles, transmission electron microscopy (TEM) studies have been carried out. In Fig. 2 we present the TEM pictures of three coated particles, corresponding to three different octadecanethiol/Fe_2O_3 mass ratios. As in all previous reports related to the sonochemical synthesis of amorphous nanoparticles [11,12,16,29,30], an agglomeration of the magnetic particles is observed, making it difficult
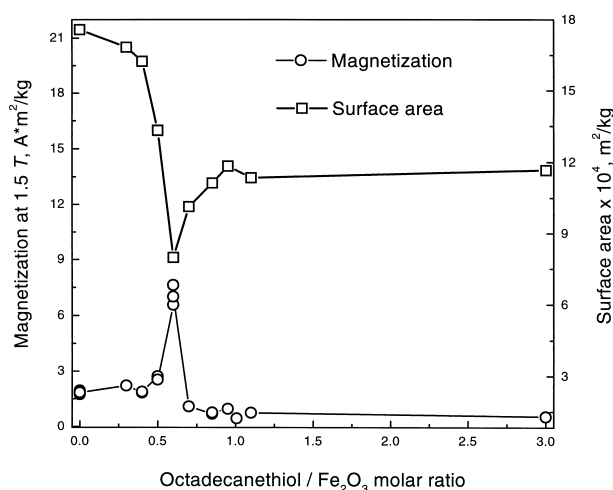
to detect the individual 2–3 nanometer-sized particles. However, qualitatively we can observe that for the thiol/Fe_2O_3 molar ratio of 0.6/1, a larger and denser agglomeration than that of 0.3/1 and 3/1 is observed. The materials on images corresponding to the 0.3/1 and 3/1 molar ratios look more porous and less agglomerated. Using the measured surface area, the theoretical calculations of particle size for spherical nanoparticles were performed. These calculations result in the nanoparticles' radius of about 3, 8 and 5 nm, for corresponding molar ratios.

2.3. Magnetic measurements

To elucidate the effect of the alkanethiol concentration on the average size of the nanoparticles during the coating process, magnetic measurements were conducted. Fig. 3 depicts the room temperature magnetization (VSM, Oxford Instrument) versus the applied magnetic field for several Fe_2O_3 nanoparticles coated with octadecanethiol, as compared to that for non-coated Fe_2O_3. All the amorphous nanosized materials show no hysteresis, and the magnetization does not saturate even at 1.5 T. Fig. 4 presents the results of room temperature magnetization (at 1.5 T) as a function of the octadecanethiol/Fe_2O_3 molar ratio. The changes observed for the magnetization are strongly correlated with the surface area and the TEM data; namely, an increase in the magnetization corresponds to a decrease of the surface area. The maximum in the magnetization is obtained at a molar ratio of 0.6/1.

In order to verify that measured magnetization is not a collective effect (i.e. there is no magnetic hysteresis), we have also performed measurements of the temperature dependence of the magnetic moment, using a SQUID magnetometer (Quantum Design). In this experiment a sample was first cooled in zero magnetic field. Then, 50 mT magnetic field was turned on and magnetic moment was measured during warming. After that, magnetic moment was measured during cooling in the presence of magnetic field. Our results, depicted in Fig. 5, reveal that above 70 K (called blocking temperature) the material exhibits magnetically reversible superparamagnetic behavior. Such value of the blocking temperature corresponds to Fe_2O_3 nanoparticles of size in a range 10–30 nm. The TEM study of our samples shows that the powder is typically a porous agglomerate of 20–30 nm particles.

3. Discussion

In previous research, nanosized particles of two main types are described: non-magnetic, small particles of metals such as gold [4,21,31–33] or copper [23], and nanoparticles of magnetic metals [5,6,8,9]. Nanoparticles of both types were deliberately isolated, so that interaction between separated particles could be prevented and agglomeration could be prohibited. In all cases described, changing the relative amounts of reactants determined the average size of the
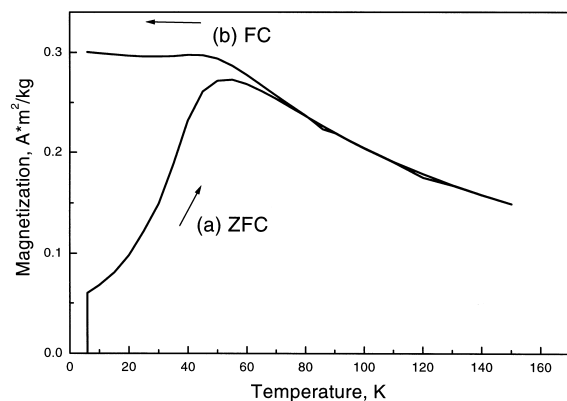

Fig. 4. Magnetization as a function of the octadecanethiol/Fe_2O_3 molar ratio in the coating solution. For comparison, the surface area as a function on the thiol/oxide molar ratio is plotted (dashed line).

Fig. 5. Magnetization versus the temperature: (a) zero-field cooling (ZFC), (b) field cooling (FC) in magnetic field 50 mT.

Fig. 7. Sulfur content versus the molar ratio of octadecanethiol/Fe_2O_3 in the coating solution, as deduced from the elemental analysis.

dispersed substance, and a decrease in the particle size, together with a concomitant increase in surfactant concentration, was also observed.

In our case, the obtained powder consists of 10–20 nano-sized ferromagnetic particles. Due to magnetic interaction, they tend to agglomerate, which is possible because the particles are mobile when the material is dispersed in a coating solution. The role of the surfactant is dual. At low concentrations, the surfactant provokes agglomeration due to lowering of the energy of the coated surface, so that the system tends to reduce the total surface area. The strength of this factor is proportional to the amount of the surfactant with respect to any given amount of the non-coated material. On the other hand, the coated surface becomes inactive, which inhibits agglomeration. Since a larger amount of the surfactant allows for coating of the larger surface, this factor limits the size increase of the particles. These two opposing factors determine the role of the surfactant in the arrangement of the coated nanoparticles, i. e. we may expect to find a non-monotonous dependence of the particle size on the surfactant concentration. In particular, at low concentrations of the surfactant, an increase in its quantity leads to accel-
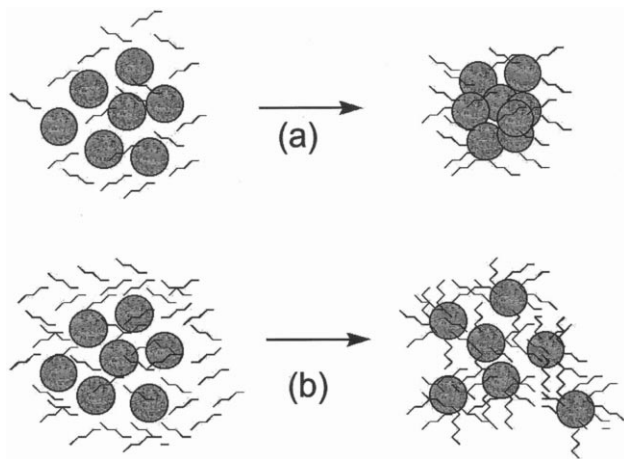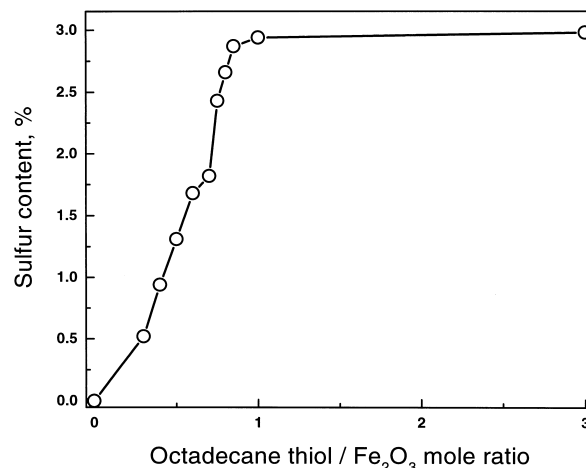
eration of the aggregation, whereas the total coated surface remains small. At some critical level of surfactant quantity, all the agglomerates are coated, hence stabilized. Further increase of the surfactant concentration can only reduce the size of the agglomerates, which finally allows for coating of all the initial particles. This results in the non-monotonous dependence of both the total surface area and the magnetization on the amount of the surfactant in the system, as demonstrated in Fig. 4. The point of inflection corresponds to the highest level of agglomeration of the nanoparticles, and to the lowest total surface area. This state corresponds to the full monolayer coverage of the aggregates. The maximal magnetization and the minimal area appear at the same octadecanethiol/oxide molar ratio, namely 0.6/1. The scheme of the coating process in the presence of various amounts of surfactant depicted in Fig. 6, illustrates the given above explanation.

Our explanation is supported by elemental analysis of the sulfur content. At low proportions between the thiol and oxide, the percentage of sulfur atoms grows, and then, at a molar ratio of about 0.9/1–1.0/1, it reaches a constant value (see Fig. 7). This means that for a molar ratio above 1.0/1, thiol will not be chemically bound to the iron oxide surface and will form a multilayer. The excess molecules may be removed by the annealing process in a vacuum, at 80–90°C [33].

Similarly, the amorphous iron was coated with octadecanethiol, and the same measurements were repeated as a function of the thiol/Fe molar ratio. Similar non-monotonous behavior was observed both for magnetization and surface area.

Fig. 6. Schematic diagram of coating in the presence of: (a) low amount of thiol, (b) large amount of thiol.

4. Conclusions

The average size of the SA-coated amorphous nanoparticles is controlled by the concentration of surfactant in the

coating solution. The maximal magnetization and the minimal total area are found for nanoparticles coated with the same molar ratio of octadecanethiol/oxide in the coating solution, namely of 0.6/1. Before this critical ratio the magnetization increases and total surface area decreases with the increase of the surfactant concentration, whereas after this ratio the trend is opposite. The observed dependence of the magnetic properties on the thiol/Fe_2O_3 molar ratio is of great importance because it might lead to the ''tailoring'' of magnetic properties of coated nanoparticles.

Acknowledgements

References

[1] N. Ichinose, Superfine particle Technology, Spring-Verlag, Berlin, 1992.

[2] L. Yiping, G.C. Hadjipanayis, G.M. Sorenson, J. Klabunde, J. Magn. Magn. Mater. 104 (1992) 1545.

[3] F.J. Lazaro, J.L. Carcia, V. Schnunemann, A.X. Trautwein, IEEE Trans. Magn. 29 (1993) 2652.

[4] J. Turkevich, P.C. Stevenson, J. Hiller, J. Discuss. Faraday Soc. 11 (1951) 55.

[5] J.P. Chen, K.M. Lee, C.M. Sorensen, K.J. Klabunde, G.C. Hadjipanayis, J. Appl. Phys. 75 (1994) 5876.

[6] J.P. Chen, C.M. Sorensen, K.J. Klabunde, G.C. Hadjipanayis, J. Appl. Phys. 75 (1994) 6316.

[7] K.J. Davies, S. Wells, R.V. Upadhyay, S.W. Charles, K.O. O, rsquo;-Grady, M. El Hilo, T. Meaz, S.J. Morup, J. Magn. Magn. Mater. 149 (1995) 14.

[8] N. Moumen, P. Veillet, M.P. Pileni, J. Magn. Magn. Mater. 149 (1995) 67.

[9] N. Moumen, M.P. Pileni, J. Phys. Chem. 100 (1996) 1867.

[10] N.S. Kommareddi, M. Tata, V.T. John, et al., Chem. Mater. 8 (1996) 801.

[11] K.S. Suslick, S.B. Choe, A.A. Cichowlas, M.W. Grinstaff, Nature 353 (1991) 414.

[12] K.S. Suslick, M. Fang, T. Hyeon, A.A. Cichowlas, in: K.E. Gonsalves (Ed.), Molecularly Designed Nanostructered Materials, M.R.S, Pittsburgh, PA, 1994.

[13] K.S. Suslick, T. Hyeon, Chem. Mater. 8 (1996) 2172.

[14] K.S. Suslick, M. Fang, T. Heyon, J. Am. Chem. Soc. 118 (1996) 11960.

[15] Y. Koltypin, G. Kataby, X. Cao, R. Prozorov, A. Gedanken, J. Non-Cryst. Solid. 201 (1996) 159.

[16] X. Cao, Y. Koltypin, R. Prozorov, G. Kataby, I. Felner, A. Gedanken, J. Mater. Res. 12 (1997) 402.

[17] K.V.P.M. Shafi, R.B. Goldfarb, A. Gedanken, J. Appl. Phys. 81 (1997) 6901.

[18] K.V.P.M. Shafi, Y. Koltypin, A. Gedanken, R. Prozorov, J. Balogh, J. Lendvai, I. Felner, J. Phys. Chem. 101 (1997) 6409.

[19] A. Ulman, R.P. Scaringe, Langmuir 8 (1992) 894.

[20] Q. Liu, Z. Xu, Langmuir 11 (1995) 4617.

[21] G. Frens, Nature Phys. Sci. 241 (1973) 20.

[22] K.J. Davies, S. Wells, S.W. Charles, J. Magn. Magn. Mater. 122 (1993) 24.

[23] I. Lisiecki, F. Billoudet, M.P. Pileni, J. Phys. Chem. 100 (1996) 4160.

[24] D.V. Leff, P.C. O, rsquo;Hara, J.R. Heath, W.M. Gelbart, J. Phys. Chem. 99 (1995) 7036.

[25] O. Rozenfeld, Y. Koltypin, H. Bamnolker, S. Margel, A. Gedanken, Langmuir 10 (1994) 3919.

[26] G. Kataby, Y. Koltypin, Y. Rothe, J. Hormes, I. Felner, X. Cao, A. Gedanken, Chem. Mater. (1998) submitted(1998).

[27] G. Kataby, T. Prozorov, Y. Koltypin, C.N. Sucenik, A. Ulman, A. Gedanken, Langmuir 13 (1997) 6151.

[28] G. Kataby, A. Ulman, R. Prozorov, A. Gedanken, Langmuir 14 (1998) 1512.

[29] M.W. Grinstaff, M.B. Salamon, K.S. Suslick, Phys. Rev. B 48 (1993) 269.

[30] K.E. Gonsalves, S.P. Rangarajan, A. Garcia-Ruiz, C.C. Law, J. Mater. Sci. Lett. 15 (1996) 1261.

[31] M. Brust, M. Walker, D. Bethell, D.J. Shiffrin, R. Whyman, J. Chem. Soc. Chem. Commun. 801 (1994).

[32] M. Brust, J. Fink, D. Bethell, D.J. Shiffrin, C. Kiely, J. Chem. Soc. Chem. Commun. 1655 (1995) 1.

[33] C.S. Weisbecker, M.V. Merritt, G.M. Whitesides, Langmuir 12 (1996) 3763.